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(54) **Silver halide photographic emulsion.**

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JOURNAL OF IMAGING SCIENCE, vol. 29, no. 5, September/October 1985, pages 193-195, Society of Photographic Scientists and Engineers, Springfield, Virginia, US; S. BANDO et al.: "Photographic silver halide emulsion containing double structure grains"

(73) Proprietor: **KONICA CORPORATION**
26-2, Nishishinjuku 1-chome, Shinjuku-ku
Tokyo 160(JP)

(72) Inventor: **Ishikawa, Sadayasu Konica Corporation**
1 Sakura-machi
Hino-shi Tokyo(JP)
Inventor: **Tsukamoto, Masaru Konica Corporation**
1 Sakura-machi
Hino-shi Tokyo(JP)
Inventor: **Yagi, Toshihiko Konica Corporation**
1 Sakura-machi
Hino-shi Tokyo(JP)

(74) Representative: **Brock, Peter William et al**
URQUHART-DYKES & LORD 91 Wimpole Street
London W1M 8AH(GB)

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Description

FIELD OF THE INVENTION

This invention relates to a novel silver halide emulsion and m re particularly to a silver halide emulsion which is excellent in development activity, gamma and processing stability.

BACKGROUND OF THE INVENTION

In recent years, there have been increasing demands for the characteristics of photographic silver halide emulsions and,in particular, the demands have been highly leveled up for the photographic characteristics such as high sensitivity, low fogging and high gamma.

It has become essential to provide stable photographic characteristics against the variations in photographic conditions. In particular, it has been strongly demanded to make both sensitivity and contrast stable against the variations of various factors required in processing steps, such as the quantity of light-sensitive materials to be processed, the amount of a developer to be replenished, a temperature of the developer to be used and a processing time to be taken.

To meet these demands, there have been the proposals for highly sensitive emulsions having a high silver iodide content inside of the grains and a distinct core/shell structure in the grains thereof. These proposals were disclosed in, for example, Japanese Patent Publication Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. Publication) Nos. 143331-1985, 3247-1987 and 7039-1987.

With these emulsions, the developability thereof are not so good because a total average of silver iodide contents is relatively high and the contrasts may hardly be controlled within a certain developing time. Besides the above, there has also been a proposal for a silver halide emulsion in which a total average of silver iodide contents is lowered by reducing the silver iodide content of each core as the distinct core/shell structure remains unchanged. This proposal was disclosed in one of the examples given in Japanese Patent O.P.I. Publication No. 143331-1985. However, this emulsion deteriorates its pressure resistance property, though its development activity may be improved.

On the other hand, Japanese Patent O.P.I. Publication Nos. 35726-1985 and 147727-1985 disclose the technologies in which a high silver iodide content is provided to the cores of core/shell emulsion grains so as to reduce the total average silver iodide content of the emulsion. However, this emulsion has not any distinct core/shell-structure and, therefore, a high sensitization may hardly be achieved.

In the conventional technologies, as mentioned above, it has been difficult to materialize a silver halide emulsion which is excellent in development activity and ready in contrast control, without detriorating both sensitivity and pressure resistance property.

EP-A-0147868 discloses a light-sensitive silver iodobromide emulsion containing core/shell silver iodobromide grains having a core substantially comprising silver iodobromide containing at least about 5 mol% of silver iodide and a shell selected from the group consisting of (a) a shell comprising silver iodobromide having a lower silver iodide content than that of the silver iodobromide of the core and (b) a shell comprising silver bromide, wherein the relative standard deviation of the silver idodide content of the individual grains of said silver halide emulsion is lower than about 20%.

It is, therefore, an object of the invention to provide a silver halide photographic emulsion which is excellent in development activity, ready in contrast control and excellent in processing stability, without deteriorating both sensitivity and pressure resistance property.

According to the present invention there is provided a silver halide photographic emulsion containing core/shell type silver halide grains each comprising a core essentially consisting of silver iodobromide and at least one shell essentially consisting of silver iodobromide or silver bromide, wherein said silver halide grains have an average silver iodide content of less than 7 mol %, and said core has a silver iodide content of not less than 10 mol %, and an outermost shell has a silver iodide content of not more than 5 mol %, said silver halide grains having a size distribution of not more than 20 %, characterized in that said grains provide an X-ray diffraction pattern having at least two peaks, corresponding to said core and to said outermost shell respectively, with a diffraction angle 2θ of between 71° and 74° when a diffraction pattern of a (420) face of said grains is measured using a powder X-ray diffraction method with K α rays of Cu, and a ratio of the lowest intensity between said peaks to the highest intensity of the lowest peak of said peaks of 0.7 or less.

Each of the core/shell type grains which ar to be contained in the emulsions of th invention is comprised of both of a core for serving as the nucleus of the grain and a shell for covering the core, and

the shell is formed into one or more layers. It is preferable that the silver iodide contents of both cores and shells should be different from each other and, it is particularly pr ferable that the grains should be so formed as to mak the silver iodide contents of th cores be the highest comprising to those of the other portions of the grains.

In the invention, the above-mentioned cores are to have a silv r iodide content of not less than 10 mol%, however, preferably from 10 to 40 mol%, mor preferably from 15 to 40 mol% and particularly from 20 to 40 mol%. Among the above-mentioned shells, a shell arranged to the outermost side, i.e., the outermost surface shell, is to have a silver iodide content of not more than 5 mol%, however, preferably less than 4 mol% and more preferably from 0 to 2.0 mol%.

A core proportion to the whole body of a grain should be desirably from 2 to 60% and more preferably from 5 to 50%.

In the silver halide grains of the invention, when the silver iodide content of the core and that of the shell are different from each other, it is preferable to provide a sharp interface between the core portion having a high silver iodide content and the shell portion having a low silver iodide content. It is also preferable to interpose, between the core and shell, at least one intermediate layer having a silver iodide content which is medium between those of the cores and the outermost surface shell.

When an emulsion of the invention is comprised of the core/shell type silver halide grains having the above-mentioned intermediate layer, the preferable proportion by volume of the intermediate layer should be from 1 to 30% of the whole grains and more preferably from 5 to 20% thereof.

The differences of silver iodide contents both between a shell and the intermediate layer and between the intermediate layer and the core should be preferably not less than 3 mol%, respectively, and the difference of silver iodide contents between the core and a shell should be not less than 10 mol%.

In the silver halide photographic emulsions of the invention, the average silver iodide content thereof is to be 5 less than 7 mol%, preferably not more than 6 mol%, more preferably less than 5 mol% and most preferably from 0.5 to 4 mol%.

As mentioned above, the emulsions of the invention are to be those mainly containing silver iodobromide. It is, however, allowed to contain silver halides having the other composition such as silver chloride, provided that the advantages of the invention may not be spoiled.

When a core/shell type silver halide grain is grown initially from a seed grain, as disclosed in Japanese Patent O.P.I. Publication Nos. 177535-1984 and 138538-1985, there may be some instances where some area in the center of the grain may have a halide composition different from that of the core of the grain. If this is the case, for the halide compositions of the seed grain, it is allowed to use any silver halide compositions such as silver bromide, silver iodo- bromide, siler chloroiodobromide, silver chlorobromide, silver chloride and so forth. It is, however, preferable to use silver iodobromide having a silver iodide content of not more than 10 mol%, or silver bromide.

A seed emulsion proportion should be preferably not more than 50% of the whole silver halide and particularly not more than 10% thereof.

In the above-mentioned core/shell type silver halide grains, a silver iodide distribution may be detected in various physical measurement methods. For example, the detection may be made in such a low-temperature luminescence measurement method or an X-ray diffractometry as described in The Abstracts of the Lectures given at 1981 Annual Convention of Society of Photographic Science and Technology of Japan.

The core/shell type grains contained in the emulsions of the invention each have a distinct core/ shell structure in which a core and a shell are distinct from each other. The term, a distinct core/shell structure used herein, means a structure capable of providing a diffraction curve having at least two peaks corresponding to the core and shell, respectively, within the range of diffraction angles (2θ) of from 71 to 74 degrees, such diffraction angles are measured in the undermentioned X-ray diffractometry.

Namely, in silver halide grains having a distinct core/shell structure, which are aplicable to the emulsions of the invention, the structure thereof may be measured in an X-ray diffractometry.

When a diffraction pattern of the (420) face of a silver halide is measured in a powder-radiography at a tube voltage of 40KV and a tube current of 100mA, by making use of Cu as a target and Kα rays of Cu as a radiation source, there may be obtained a diffraction curve having at least two peaks corresponding to a core and a shell respectively within the range of diffraction angles (2θ) of from 71 to 74 degrees, provided that the emulsion grains have a distinct core/shell structure. The expression, a diffraction curve has two peaks used herein, means that a ratio of the lowest intensity between the peaks to a intensity of the lowerst peak is to be not higher than 0.9. The value of this ratio is preferably, not higher than 0.7. When comparing th two peak intensiti s, the peak int nsity correspondng t a core should be preferably from 1/20 to 1/1 of the diffraction peak intensity corresponding to a shell and more preferably from 1/15 to 1/2 th reof.

It has been described before that, in the silver halide emulsion grains of the invention, each of the grains thereof may sometimes b provided betw n the cor of a grain and th shell of th out rmost layer of the grain with an int rm diate layer having an iodide cont nt diff rent from those of th core and the shell of the outermost layer of the grain. However, this description means that, if such an intermediate layer is provided and an X-ray diffraction pattern is obtained, th intermediate layer should be provided so as not to substantially affect the forms of the two peaks respectively corresponding to a high iodide containing portion and a low iodide containing portion. In other words, this description means that a grain has a core portion having a high iodide content, an intermediate layer and the shell portion of the outermost layer and at least two peaks appear to correspond to the core and the shell and, further, the lowest intensity between the peaks should be in a ratio of not higher than 0.9 to the minimum peak intencity. When comparing the intencities of the two peaks with each other, a ratio of the peak intencity of the core to the diffraction peak intensity of the shell should be preferably from 1/20 to 1/1 and more preferably from 1/15 to 1/2. Such a silver halide grain is a grain substantially having a distinct two-layered structure.

The core/shell type silver halide grains relating to the invention may be in any crystal forms including normal crystal forms such as a cube, a tetradecahedron and an octahedron, twinned crystal forms, and the mixtures thereof. However, the normal crystal forms should be preferred.

The configurations of grains after they were formed are as mentioned above. It is preferred that, in the course of forming the grains and even after each layer was formed, the configuration of the grains should be made as same as those after the grains were formed. It is further preferred that the configurations thereof should be the same in the whole step of forming the grains. (Hereinafter this phenomenon will be referred to as that 'grains have the same hysteresis of crystal habit.')

From the silver halide emulsions of the invention, any unnecessary soluble salts may be removed after silver halide grains were grown up. Or, in the emulsions of the invention, the soluble salts may be contained as they are.

When removing such salts, it is allowed to follow the methods described in, for example, Research Disclosure, No. 17643, Chapter II. To be more concrete, in order to remove soluble salts from an emulsion which was precipitated or physically ripened, it is allowed to apply a noodle-washing method to remove them by making gelatin gelled, or to apply a flocculation method to remove them by utilizing an inorganic salt, an anionic surfactant, an anionic polymer such as polystyrenesulfonic acid, or a gelatin derivative such as an acylated gelatin, a carbamoylated gelatin and so forth. In particular, a flocculation-sedimentation method using an inorganic salt and an anionic surfactant should preferably be applied as a desalting method which may be carried out after cores were prepared in the course of manufacturing the emulsions of the invention.

In the silver halide emulsions of the invention, a distinct core/shell structure may be completed in such a manner that, after the cores are prepared, salts remaining in the emulsions are thoroughly removed by washing them with water and the shells are then grown up. This procedure is particularly important to the practical emulsion preparation. In other words, if shells are grown up without removing any salts still remaining in an emulsion after cores were prepared, it is usually hard to prepare a silver halide emulsion having a distinct core/shell structure of the invention.

After washing the salts away with water and while shells are being grown, the concentration of the salts brought in from a core emulsion should be preferably not more than 1/10 of the concentration of the salts still remaining after the core emulsion is prepared, more preferably not more than 1/100 and, most preferably not more than 1/500.

While silver halide grains are being grown, it is allowed to make present such a well-known silver halide solvent as ammonia, thioether, thiourea and so forth.

In the courses of forming and/or growing silver halide grains, at least one kind of metal salts selected from the group consisting of a cadmium salt, a zinc salt, a lead salt, a thallium salt, an iridium salt including the complex salts thereof, a rhodium salt including the complex salts thereof and an iron salt including the complex salts thereof is used to add the metal ion thereof into the silver halide grains, so that these metal elements are contained in the inside of the grains and/or to the surfaces of the grains. Further, reduction-sensitization nuclei may be provided into the inside of the grains and/or to the surfaces thereof by putting the grains in a suitable reducible atmosphere.

The silver halide grains may be those forming a latent image mainly either on the surface thereof or in the inside thereof. The silver halide grains are from 0.05 to 5.0 µm in size and preferably from 0.1 to 3.0 µm.

The silver halide photographic emulsions of the invention should preferably be a monodisperse type emulsion having a narrow grain-size distribution. Any polydisperse type mulsions having a broad grain-size distribution cannot gen rally be the distinct cor /sh ll type emulsions of the invention.

Out of the whole silver halide grains of a monodisperse type silv r halid emulsion, the silver halide grains having a grain size within the range of ± 20% with respect to an average grain-siz $\bar{r}$ should be preferably contained in a proportion of not less than 60% by w ight of th whole silver halide grains, more preferably not less than 70% by weight and particularly not less than 80% by weight thereof.

Herein, an average grain size $\bar{r}$ is defined as a grain size ri obtain d when maximizing a products ni x ri^3, in which ni repres nts the frequency of the grains having a grain-size ri, and the significant figures are 3 and, in the lowest figure, the fraction of .5 and over is counted as a unit and the rest is cut away.

The expression, 'grain size' used herein, means a diameter in the case of a spherical-shaped silver halide grain, or a diameter of a circular image having the same area as that converted from the area of the projective image of a grain in the case that the grain is in the other shapes than the spherical-shape.

The grain sizes may be obtained in such a manner, for example, that the grains are photographed after they are magnified ten thousand to fifty thousand times with an electron microscope and the grain diameters or the projective areas are measured, provided that the grains to be measured should be not less than 1000 in number at random.

When a grain distribution is defined by the following formula,

$$\frac{\text{Standard deviation}}{\text{Average grain size}} \times 100 = \text{Distribution (\%)},$$

the grain distribution of the particularly preferable high grade monodisperse type emulsions of the invention is not more than 20% and more preferably not more than 15%.

An average grain size and a standard deviation are to be obtained from the above-defined grain size ri.

A monodisperse type emulsion may be prepared in such a manner that a water-soluble silver salt solution and a water-soluble halide solution are added in a seed-grain-containing gelatin solution in a double-jet method, with controlling the pAg and pH. For determining the rate of adding the solutions may be referred to Japanese Patent O.P.I. Publication NOS. 48521-1979 and 49938-1983.

The high-grade monodisperse type emulsions may be prepared by applying a method of growing the grains of an emulsion in the presence of tetrazaindene. This method is disclosed in Japanese Patent O.P.I. Publication No. 122935-1985.

The silver halide emulsions of the invention may be chemically sensitized in an ordinary method.

The silver halide emulsions of the invention may be optically sensitized to any desired wavelength regions by making use of a dye which is well-known in the photographic industry as a sensitizing dye. Such sensitizing dyes may be used independently or in combination.

EXAMPLES

Next, the invention will be described more in detail with reference to the samples given below. It is, however, to be understood that the invention shall not be limited thereto.

Example-1

A silver iodobromide emulsion containing 2.0 mol% of silver iodide was prepared in a double jet method in the conditions at 40°C, pH 8.0 and pAg 9.0. The resulted emulsion was washed with water to remove excessive salts therefrom. In the resulted emulsion, the average grain size was 0.27 µm and the grain size distribution, i.e., the standard deviation / the average grain size, was 12.0%. This emulsion was further processed to contain silver in an amount equivalent to 1200 g of silver nitrate so as to use as seed-crystal emulsion [A]. The amount of the seed crystals [A] prepared was 4160 g.

Seed crystals [A] of 1510 g were dissolved in 8 liters of an aqueous 1% gelatin solution with keeping a temperature at 40°C, and then 0.4N-rated aqueous ammonia was added, and stirred. To the solution, 250 cc out of 2.39 liters of an aqueous solution dissolved therein with 849 g of silver nitrate were added by taking 10 minutes. The pAg and pH of the resulted solution were then adjusted to be 7.1 and 9.9, respectively. Successively, the silver nitrate solution and 2.14 liters of an aqueous 1% gelatin solution dissolved therein with both 367 g of potassium bromide and 224 g of potassium iodide were supplied at an adding rate without causing any formation of new crystal nucleus. Thus, a core emulsion containing 30 mol% of silver iodide was prepared. After the solutions wer added completely, th pH of the mulsion was reduced to 6.0 with keeping a temperature at 40°C and was then washed with water so as to r move

excessive salts.

In the washing step, 500 cc of a solution of 5% Demol (manufactured by Kao-Atlas Company) were added to 16 liters of the core emulsion with stirring. After the solution was stirred for three minutes, it was allowed to stand for five minutes so that the emulsion was flocculated and sedimented. Thereafter, 14.9 liters of the supernatant liquid not containing any emulsion were removed by means of decantation. To the remaining emulsion, 8 liters of pure water warmed up to 40°C were added, and they were stirred for four minutes. Then, 500 cc of a 20% magnesium sulfate solution were added and further stirred for three minutes, and then stopped to stirr. The resulted solution was allowed to stand for five minutes to flocculate and sediment the emulsion. 85 liters of the super- natant liquid not containing any emulsion was removed by means of decantation. To the remaining emulsion, 8 liters of pure water wamed up to 40°C were added. The above-mentioned procedures were repeated and then 1.6 liters of a 8% gelatin solution and a small amount of an antiseptic were added.

The emulsion obtained was an octahedral emulsion that contained octahedral grains. The average grain size and grain size distribution thereof were 0.378 µm and 12.3%, respectively. This emulsion is named Core Emulsion [B]. The amount of Core Emulsion [B] prepared was 4160 g and the salt concentration was 1/1290 of that of the core emulsion prepared.

Next, 817 g of Core Emulsion [B] were dissolved in 8.6 liters of an aqueous 1% gelatin solution kept at 40°C. Then, 0.61N-rated aqueous ammonia was added, and stirred. To the resulted solution, both 2.7 liters of an aqueous solution of 965 g of silver nitrate and 2.7 liters of an aqueous 1% gelatin solution of 623 g of potassium bromide were added by taking 30 minutes. The pAg and pH of the resulted solution which was in the course of the above-mentioned additions were so controlled as to be 9.7 and 8.8 at the beginning of the additions and 10.5 and 8.0 at the completion of the additions, respectively, so that the silver bromide shells were prepared on the cores. Thus obtained emulsion was washed with water in the same manner as in Core Emulsion [B] and the resulted emulsion was named Emulsion [1]. Emulsion [1] was an octa- hedral emulsion containing a total of 4.0 mol% of silver iodide. The average grain size, the grain size distribution and the amount prepared were 0.65 µm, 14.0% and 4160 g, respectively.

Further, 2083 g of Seed Crystal [A] were dissolved in 8 liters of an aqueous 1% gelatin solution kept at 40°C and Core Emulsion [C] was prepared in the same manner as in Core Emulsion [B]. The resulted emulsion was in the octahedral form. The average grain size, the grain size distribution and the amount prepared were 0.34 µm, 12.1% and 4160 g, respectively, and the salt concentration was 1/1290 of that of the core emulsion prepared. Still further, 595 g of Core Emulsion [C] were dissolved in 8.6 liters of an aqueous 1% gelatin solution kept at 40°C. Thereto, 2.88 liters of an aqueous solution containing 1028 g of silver nitrate and 2.88 liters of an aqueous 1% gelatin solution containing 716 g of potassium bromide and 5 g of potassium iodide were supplied in the same manner as in Emulsion [1] so as to prepare shells. Thus, Emulsion [2] containing a total of 4.0 mol% of silver iodide was prepared. The obtained emulsion was in the octahedral form. The average grain size, the grain size distribution and the amount prepared were 0.65 µm, 14.0% and 4160 g, respectively.

Emulsions [3] and [5] were prepared in such a manner that the core grain sizes were changed in the same manner as in Core Emulsion [B] and the silver bromide shells were grown up in the same manner as in Emulsion [1]. Emulsion [3] was an octahedral emulsion containing a total of 2.0 mol% of silver iodide and having an average grain size of 0.65 µm and a grain size distribution of 14.0%. Emulsion [5] was an octahedral emulsion containing a total of 6.2 mol% of silver iodide and having an average grain size of 0.65 µm and a grain size distribution of 13.0%.

Emulsions [4] and [6] were prepared in such a manner that the core grain sizes were changed in the same manner as in Core Emulsion [C] and the silver iodobromide shells were grown up in the same manner as in Emulsion [2]. Emulsion [4] was an octahedral emulsion containing a total of 2.0 mol% of silver iodide and having an average grain size of 0.65 µm and a grain size distribution of 14.0%. Emulsion [6] was an octahedral emulsion containing a total of 6.2 mol% of silver iodide and having an average grain size of 0.65 µm and a grain size distribution of 14.0%.

Now, the examples of the preparation of the comparative emulsions will be described.

For the purpose of leveling off the difference in sensitometric evaluations between the comparative emulsions and the emulsions of the invention, the preparation conditions of the comparative emulsions were so adjusted as to make the grain sizes be the same as those of the emulsions of the invention.

Following the method disclosed in Japanese Patent O.P.I. Publication No. 143331-1985, the cores containing 20 mol% of silver iodide were prepared and the silver bromide shells were then grown up, so that Emulsion [7] containing a total of 10.0 mol% of silver iodide was prepared.

Similarly, following th method disclosed in Japanese Patent O.P.I. Publication No. 143331-1985, the cores containing 6 mol% of silver iodide wer prepar d and the silv r bromide shells wer then grown up,

so that Emulsion [8] containing a total of 2.0 mol% of silver iodid was prepared.

Further, following the method disclosed in Japanese Patent O.P.I. Publication No. 147727-1985, the cores containing 40 mol% of silver iodide wer pr pared and the silver bromide shells were then grown up, so that Emulsion [9] containing a total of 3.0 mol% of silver iodide was prepared.

Similarly, following the method disclosed in Japan se Patent O.P.I. Publication No. 147727-1985, cores each containing 40 mol% of silver iodid were prepared and silver bromide sh lls were then grown up, so that Emulsion [10] containing a total of 10.0 mol% of silver iodide was prepared.

Following the method disclosed in Japanese Patent O.P.I. Publication No. 178447-1984, cores each containing 30 mol% of silver iodide were prepared and silver bromide shells were then grown up, so that Emulsion [11] containing a total of 2.0 mol% of silver iodide was prepared.

Following the method disclosed in Japanese Patent O.P.I. Publication No. 143331-1985, cores each containing 30 mol% of silver iodide were prepared and silver bromide shells were then grown up, so that Emulsion [12] containing a total of 2.0 mol% of silver iodide was prepared.

Further, following the method disclosed in Japanese Patent O.P.I. Publication No. 99433-1984, cores each containing 30 mo% of silver iodide were prepared and silver bromide shells were then grown up, so that Emulsion [13] containing a total of 2.0 mol% of silver iodide was prepared.

The structures of the above 13 kinds of emulsions thus prepared are collectively shown in Table 1.

Table 1

Emulsion (Inventive or comparative)	Formulated silver iodide content (mol%) (Core)	(Shell)	Total AgI content (mol%)	Distinct core/ shell structure	Average grain size (μm)	Grain-size distribution (%)
1 (Inventive)	30	0	4.0	Yes	0.65	14.0
2 (Inventive)	30	0.5	4.0	Yes	0.65	14.0
3 (Inventive)	30	0	2.0	Yes	0.65	14.0
4 (Inventive)	30	0.5	2.0	Yes	0.65	14.0
5 (Inventive)	30	0	6.2	Yes	0.65	13.0
6 (Inventive)	30	0.5	6.2	Yes	0.65	14.0
7 (Comparative)	42	0	14.0	Yes	0.65	25.0
8 (Comparative)	6	0	2.0	Yes	0.68	24.0
9 (Comparative)	40	0	3.0	None	0.66	24.0
10 (Comparative)	40	0	10.0	None	0.66	24.0
11 (Comparative)	30	0	2.0	None	0.65	15.0
12 (Comparative)	30	0	2.0	Yes	0.67	30.0
13 (Comparative)	30	0	2.0	None	0.66	40.0

In the column of the distinct core/shell structure of Table 1, an indication, 'Yes', represents that two diffraction peaks corresponding to a core and a shell are shown at a diffraction angle (2θ) within the range of from 71° to 74° in the aforementioned powder X-ray diffractometry, and an indication, 'None', represents the other cases than the above. In Emulsions [1] through [7] and Emulsion [12], the double-peak of a core and a shell were apparently found. In Emulsion [8], two diffraction peaks were found, though the peaks were considerably close to each other.

In Emulsions [9], [10], [11] and [13], on the other hand, only one diffraction peak was found. From this fact, it may be judged that Emulsions [9], [10], [11] and [13] have no core/shell structure without doubt.

The above-mentioned 13 kinds of the emulsions were gold-sulfur-sensitized by adding ammonium thiocyanate, a chloroaurate and hypo, respectively. Further, to each emulsion, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene was added and the ordinary photographic additives such as a spreading ag nt, a thick ning agent, a hardening agent and so forth wer then added. Th resulted emulsions w re coated in an ordinary

method respectively onto a subbed polyethyleneterephthalate film base so that silv r may be contain d in an amount of 50 mg per 100 cm^2, and dried up. Thus, th samples f r sensitometric evaluation use w re prepared, respectively. In the sensitometric evaluation thereof, an exposure was made to a light sourc having a color temperature of 5400°K, through an optical wedge, for 1/100 of a second. The exposure quantity was 3.2 CMS.

N xt, th following processing steps were carried out.

(Processing step) (At 35°C)	(Processing time)
1. Developing	30 sec.
2. Fixing	21 sec.
3. Washing	14 sec.
4. Drying	

[Developer]	
Potassium sulfite, anhydrous	50 g
Hydroquinone	10 g
Boric acid, anhydrous	1 g
Potassium carbonate, monohydrate	15 g
1-phenyl-3-pyrazolidone	0.5 g
Potassium hydroxide	4 g
5-methyl-benzotriazole	0.05 g
Potassium bromide	5 g
Glutaraldehyde bisulfite	15 g
Glacial acetic acid	8 cc
Add water to make	1 liter

[Fixer]	
Water (at about 50°C)	600 ml
Sodium thiosulfate	240 g
Sodium sulfite, anhydrous	15 g
Glacial acetic acid	13.4 ml
Boric acid	7.5 g
Potassium alum	15 g
Add water to make	1 liter

Table 2 shows the results of the photographic characteristics of the samples prepared.

Table 2

Sample (Inventive or comparative)	Gamma	R lative sensitivity*	Pressure-resistance ** (ΔD)
1 (Inventive)	1.36	100	0.06
2 (Inventive)	1.35	105	0.07
3 (Inventive)	1.38	99	0.08
4 (Inventive)	1.32	101	0.08
5 (Inventive)	1.28	100	0.06
6 (Inventive)	1.27	101	0.07
7 (Comparative)	0.94	90	0.10
8 (Comparative)	0.95	71	0.41
9 (Comparative)	0.99	80	0.11
10 (Comparative)	0.82	82	0.14
11 (Comparative)	0.99	92	0.14
12 (Comparative)	1.02	90	0.12
13 (Comparative)	0.98	84	0.16

* Relative sensitivity: The sensitivity of Sample 1 was regarded as a relative value of 100 and those of the other samples were shown by the values relative thereto.

** Pressure resistance test: An emulsion side was folded inside at a constant speed and the above-mentioned development was carried out. In the resulted samples, the density difference (Dp-Dg) between a density (Dp) in the area darkened by folding and the ground density (Dg) was obtained. The results were shown in terms of ΔD in this table.

As is obvious from the results shown in Table 2, in Samples 1 through 6 of the invention, the high gamma values were obtained without deteriorating any sensitivity and pressure resistance.

Example-2

With respect to Samples 1 through 10, the developing temperature was changed to 35 °C ± 3 °C and they were processed as mentioned above. The resulted processing temperature dependency of each sample was evaluated. The results thereof are shown in Table 3.

Table 3

Sample (Inv. or Comp.)	Prcs. temp., 32°C			Prcs. temp., 35°C			Prcs. temp., 38°C		
	Fog	Rel. sens.	Gamma	Fog	Rel. sens.	Gamma	Fog	Rel. sens.	Gamma
1 (Inv.)	0.03	98	1.35	0.03	100	1.36	0.04	103	1.37
2 (Inv.)	0.03	102	1.34	0.03	105	1.35	0.04	106	1.36
3 (Inv.)	0.03	98	1.36	0.03	99	1.38	0.04	103	1.39
4 (Inv.)	0.03	100	1.30	0.03	101	1.32	0.04	104	1.34
5 (Inv.)	0.03	94	1.24	0.04	100	1.28	0.05	102	1.28
6 (Inv.)	0.04	95	1.23	0.05	101	1.27	0.06	103	1.29
7 (Comp.)	0.09	87	0.70	0.15	90	0.94	0.20	93	0.96
8 (Comp.)	0.02	61	0.81	0.04	71	0.95	0.07	80	1.00
9 (Comp.)	0.02	71	0.76	0.04	80	0.99	0.07	94	1.10
10 (Comp.)	0.02	64	0.60	0.05	82	0.82	0.09	90	0.95
11 (Comp.)	0.02	90	0.93	0.03	92	0.99	0.04	98	1.16
12 (Comp.)	0.03	87	0.96	0.04	90	1.02	0.05	96	1.18
13 (Comp.)	0.03	79	0.92	0.05	84	0.98	0.07	90	1.12

As is obvious from the results shown in Table 3, the following facts were found. Namely, in the comparative samples, the characteristic variations thereof were seriously affected by the processing temperature variations. In Samples 1 through 6 of the invention, the dependencies of fogginess, sensitivity and gamma upon processing temperature were relatively small and the processing stability was improved. Further, in Samples 1 through 6, a high sensitivity and a high gamma can be obtained even at a processing temperature of 32°C. From these facts, it is, therefore, understood that the photographic emulsions of the invention are excellent in development activity.

Furthermore, the contrasts of the emulsions of the invention may readily be controlled when preparing th m, because the gamma values th reof are stable regardl ss of proc ssing temperatures.

As described above, the silver halid photographic emulsions of the invention are exc llent in

development activity, ready in controlling contrasts and also excellent in processing stability, without d terioratlng any sensitivity and pr ssure resistance.

Claims

1. A silver halide photographic emulsion containing core/shell type silver halide grains each comprising a core essentially consisting of silver iodobromide and at least one shell essentially consisting of silver iodobromide or silver bromide, wherein said silver halide grains have an average silver iodide content of less than 7 mol %, and said core has a silver iodide content of not less than 10 mol %, and an outermost shell has a silver iodide content of not more than 5 mol %, said silver halide grains having a size distribution of not more than 20 %, characterized in that said grains provide an X-ray diffraction pattern having at least two peaks, corresponding to said core and to said outermost shell respectively, with a diffraction angle 2θ of between 71° and 74° when a diffraction pattern of a (420) face of said grains is measured using a powder X-ray diffraction method with Kα rays of Cu, and a ratio of the lowest intensity between said peaks to the highest intensity of the lowest peak of said peaks of 0.7 or less.

2. The emulsion according to claim 1, characterized in that said core has a silver iodide content of from 10 mol % to 40 mol %.

3. The emulsion according to claim 2, characterized in that said core has a silver iodide content of from 15 mol % to 40 mol %.

4. The emulsion according to claim 3, characterized in that said core has a silver iodide content of from 20 mol % to 40 mol %.

5. The emulsion according to claim 1, characterized in that said outermost shell has a silver halide content of less than 4 mol %.

6. The emulsion according to claim 5, characterized in that said outermost shell has a silver halide content of from 0 to 2.0 mol %.

7. The emulsion according to claim 1, characterized in that said average silver iodide content is not more than 6.0 mol %.

8. The emulsion according to claim 7, characterized in that said average silver iodide content is not more than 5.0 mol %.

9. The emulsion according to claim 7, characterized in that said average silver iodide content is from 0.5 to 4 mol %.

10. The emulsion according to any of the preceding claims, characterized in that the ratio of the intensity said peak corresponding to the core to the intensity of said peak corresponding to the shell is from 1/20 to 1/1.

11. The emulsion according to claim 10, characterized in that the ratio of the intensity said peak corresponding to the core to the intensity of said peak corresponding to the shell is from 1/15 to 1/2.

Patentansprüche

1. Photographische Silberhalogenidemulsion mit Silberhalogenidkörnern vom Kern/Schalentyp, die je einen im wesentlichen aus Silberjodbromid bestehenden Kern und mindestens eine im wesentlichen aus Silberjodbromid oder Silberbromid bestehende Schale enthalten, wobei diese Silberhalogenidkörner einen durchschnittlichen Silberjodidgehalt von weniger als 7 Mol-%, jener Kern einen Silberjodidgehalt von nicht weniger als 10 Mol-% sowie eine äußerste Schale einen Silberjodidgehalt von nicht mehr als 5 Mol-% aufweisen, wobei die Größenverteilung der Silberhalogenidkörner nicht mehr als 20 % beträgt, dadurch gekennzeichnet, daß di se Körner ein Röntgenbeugungsmuster mit mindestens zwei Spitzen rgeben, die zu jenem Kern bzw. jener äußersten Schale g hören, mit einem Beugungswinkel

2θ zwischen 71° und 74° bei Messung des Beugungsmust rs einer 420-Fläche der Körner nach einer Röntgenpulverbeugungsmethode mit Cu-K_α-Strahlung, wobei das Verhältnis d r kl insten Intensität zwischen diesen Spitzen zur höchsten Intensität d r niedrigsten Spitze dieser Spitzen 0,7 oder weniger beträgt.

2. Emulsion nach Anspruch 1, dadurch gekennzeichnet, daß dieser Kern einen Silberjodidgehalt von 10 bis 40 Mol-% aufweist.

3. Emulsion nach Anspruch 2, dadurch gekennzeichnet, daß dieser Kern einen Silberjodidgehalt von 15 bis 40 Mol-% aufweist.

4. Emulsion nach Anspruch 3, dadurch gekennzeichnet, daß der Kern einen Silberjodidgehalt von 20 bis 40 Mol-% aufweist.

5. Emulsion nach Anspruch 1, dadurch gekennzeichnet, daß jene äußerste Schale einen Silberhalogenidgehalt von weniger als 4 Mol-% aufweist.

6. Emulsion nach Anspruch 5, dadurch gekennzeichnet, daß diese äußerste Schale einen Silberhalogenidgehalt von 0 bis 2,0 Mol-% aufweist.

7. Emulsion nach Anspruch 1, dadurch gekennzeichnet, daß der durchschnittliche Silberjodidgehalt nicht mehr als 6,0 Mol-% beträgt.

8. Emulsion nach Anspruch 7, dadurch gekennzeichnet, daß der durchschnittliche Silberjodidgehalt nicht mehr als 5,0 Mol-% beträgt.

9. Emulsion nach Anspruch 7, dadurch gekennzeichnet, daß der durchschnittliche Silberjodidgehalt 0,5 bis 4 Mol-% beträgt.

10. Emulsion nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Intensitätsverhältnis der zum Kern gehörenden Spitze zu der zur Schale gehörenden Spitze 1/20 bis 1/1 beträgt.

11. Emulsion nach Anspruch 10, dadurch gekennzeichnet, daß das Intensitätsverhältnis jener zum Kern gehörenden Spitze zu der zur Schale gehörenden Spitze 1/15 bis 1/2 beträgt.

Revendications

1. Emulsion photographique à l'halogénure d'argent contenant des grains d'halogénure d'argent de type à noyau/enveloppe comprenant chacun un noyau essentiellement constitué d'iodobromure d'argent et au moins une enveloppe essentiellement constituée d'iodobromure d'argent ou de bromure d'argent, dans laquelle lesdits grains d'halogénure d'argent ont une teneur moyenne en iodure d'argent inférieure à 7% en moles et ledit noyau a une teneur en iodure d'argent d'au moins 10% en moles, et l'enveloppe externe a une teneur en iodure d'argent d'au plus 5% en moles, lesdits grains d'halogénure d'argent ayant une distribution granulométrique d'au plus 20%, caractérisée en ce que lesdits grains donnent un diagramme de diffraction des rayons X possédant au moins deux pics, qui correspondent respectivement audit noyau et à ladite enveloppe externe, avec un angle de diffraction 2θ compris entre 71° et 74° lorsqu'on mesure le diagramme de diffraction d'une face (420) desdits grains en employant une méthode de diffraction des rayons X sur poudre avec le rayonnement K_α du Cu, et le rapport de la plus faible intensité entre lesdits pics à la plus forte intensité du pic le plus faible desdits pics est inférieur ou égal à 0,7.

2. Emulsion selon la revendication 1, caractérisée en ce que ledit noyau a une teneur en iodure d'argent de 10% en moles à 40% en moles.

3. Emulsion selon la revendication 2, caractérisée en ce que ledit noyau a une teneur en iodure d'argent de 15% en moles à 40% en moles.

4. Emulsion selon la revendication 3, caractérisé en ce que ledit noyau a une ten ur en iodure d'argent

de 20% en moles à 40% en moles.

5. Emulsion selon la revendication 1, caractérisée n ce que ladite enveloppe externe a une teneur en halogénure d'argent inférieure à 4% en moles.

6. Emulsion selon la revendication 5, caractérisée en ce que ladite env loppe externe a un teneur en halogénure d'argent de 0 à 2,0% en moles.

7. Emulsion selon la revendication 1, caractérisée en ce que ladite teneur moyenne en iodure d'argent n'est pas supérieure à 6,0% en moles.

8. Emulsion selon la revendication 7, caractérisée en ce que ladite teneur moyenne en iodure d'argent n'est pas supérieure à 5,0% en moles.

9. Emulsion selon la revendication 7, caractérisée en ce que ladite teneur moyenne en iodure d'argent est de 0,5 à 4% en moles.

10. Emulsion selon l'une quelconque des revendications précédentes, caractérisée en ce que le rapport de l'intensité dudit pic correspondant au noyau à l'intensité dudit pic correspondant à l'enveloppe est de 1/20 à 1/1.

11. Emulsion selon la revendication 10, caractérisée en ce que le rapport de l'intensité dudit pic correspondant au noyau à l'intensité dudit pic correspondant à l'enveloppe est de 1/15 à 1/2.